



## PATENT SPECIFICATION

NO DRAWINGS

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C3 R(22C6X, 22D1A2, 22D2A2)

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## COMPLETE SPECIFICATION

**Polyolefin- and Polyamide-Containing Compositions**

We, BERK LIMITED, formerly known as F. W. Berk & Company Limited, a British Company of Berk House, 8 Baker Street, London, W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyolefin and polyamide-containing compositions and to the preparation thereof. The synthetic thermoplastic polyolefin and polyamide compositions customarily used for the fabrication of articles by procedures such as moulding and extrusion, contain little or no plasticiser and the polyolefin and polyamide compositions referred to in the present specification are those containing no plasticiser or not more than 5% of plasticiser based on the weight of the polymer.

The processing of such polyolefin and polyamide compositions may be subject to difficulties arising from the particular rheological properties of the polymer at the processing temperature employed. For example, certain of these polymers, such as nylon 6,6, have a "sharp" melting point and, as a result, some shaping procedures commonly used in plastics technology cannot satisfactorily be used with these polymers without considerable and expensive modifications of the equipment used.

We have found that useful modifications in the rheological properties of polyolefins and polyamides whilst in a plastic state, can be obtained by incorporating in the polymers a small proportion (that is less than about 10%, based on the weight of the polymer) of an organophilic cation modified clay.

According to the present invention, therefore, we provide a polymer composition which comprises, as major component, a synthetic thermoplastic polyolefin or polyamide and up to 10%, based on the weight of the polymer, of an organophilic cation modified clay.

The nature of the modification in the rheological properties of the polymer will

depend on the nature of the latter. Thus the softening characteristics of the polymers referred to above which have a "sharp" melting point can be sufficiently modified by the incorporation of an organophilic cation modified clay to enable the polymers to be shaped in standard equipment.

Polyolefins, such as polyethylene and polypropylene, and polyamides, such as nylon 6,6, drip or flow readily when heated beyond their softening point and this characteristic increases the fire hazard presented by these polymers; the tendency to flow can, however, be substantially reduced by the incorporation of an organophilic cation modified clay in such polymers.

Suitable organophilic cation modified clays for incorporation in the polymers are cationic clays of medium or high cation exchange capacity, the cation of which is replaced by a so-called onium base. The onium base may contain a pentavalent atom as in the cases of ammonium, phosphonium, arsonium and stibonium bases; a tetravalent atom as in the cases of oxonium, sulphonium, selenonium, telluronium and stannonium bases; or a trivalent atom as in the case of an iodonium base. The cation exchange capacity is generally reported as the number of milliequivalents of exchangeable base which can be exchanged per 100 grams of clay dried at 105°C. The cationic clays have very different cation exchange capacities, the numerical values varying from about 3 to about 120 depending upon the type of clay. On this basis clays have been divided empirically into those of low cation exchange capacity, i.e. up to about 15; those of medium cation exchange capacity, i.e. above 15 but below 40; and those of high cation exchange capacity, i.e. 40 and above.

Examples of clays having a medium cation-exchange capacity are sepiolite and attapulgite. Examples of clays having a high cation-exchange capacity are the montmorillonites,

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such as sodium, potassium, lithium and other bentonites, particularly those of the Wyoming and South Dakota (U.S.A.) types and magnesium bentonite (which is also known as hectorite), saponite and nontronite. Certain so-called "synthetic clays" are also known and provided that they are equivalent to the natural clays described above in their ability to react with onium compounds, they are suitable.

Details of the preparation of organophilic cation modified clays are given, for instance, in British Specification No. 664,830 and U.S. Patent No. 2,531,440. If desired, the sodium ion content of the clay may be increased prior to reaction with the onium compound as described in British Specification No. 904,880.

Specific examples of suitable organophilic cation modified clays are: dimethyl dioctadecyl ammonium sepiolite, octadecyl ammonium montmorillonite, dimethyl dioctadecyl ammonium montmorillonite, and dimethyl dioctadecyl ammonium hectorite.

Another class of organophilic cation modified clays that can be used are cationic clays of high cation-exchange capacity, e.g. montmorillonites, which are associated with an aliphatic amine containing at least 12 carbon atoms, such as dodecylamine, octadecylamine, methyloctadecylamine, dioctadecylamine and dimethyloctadecylamine, or a derivative thereof, for example the derivatives of such amines obtained by fusing them with a non-ionic, long chain, organic polar compound, such as stearamide, stearonitrile and cetyl alcohol.

The proportion of organophilic cation modified clay incorporated in the polymer is preferably from 0.5 to 5%, based on the weight of the polymer, although higher proportions may be desirable in some cases.

The polymer compositions can also, of course, contain one or more anti-oxidants, stabilisers, anti-static agents, fillers, pigments and the like.

The organophilic cation modified clay can be added as a dry powder directly to the polyolefin or polyamide during processing of the polymer. If desired, the organophilic cation modified clay may be dispersed in a volatile liquid organic vehicle prior to incorporation in the polymer; examples of such vehicles include trichloroethylene, toluene, xylene and white spirit. A masterbatch of polymer and organophilic cation modified clay may be used as the method of introducing the organophilic cation modified clay; such a masterbatch may be made by dispersing the organophilic cation modified clay in a volatile liquid organic vehicle, such as toluene, and then incorporating the dispersion in a proportion of polymer. The volatile organic liquid vehicle may be substantially completely removed prior to or during processing of the polymer. The organophilic cation modified clay may, on the other hand, be dispersed in a relatively non-volatile vehicle including, for

instance, the additives for the polymer, and vehicles such as paraffin wax and a low molecular weight polyethylene. In such cases the vehicle remains in the polymer after processing and may be referred to as a "dispersant". Additionally, the use of an organophilic cation modified clay dispersed in a non-volatile vehicle may be accompanied by the addition of a volatile liquid organic vehicle which may be substantially completely removed prior to or during processing of the polymer. For best results the modified clay is treated with an organic polar liquid prior to its incorporation in the polymer. Methanol has been found to be suitable for this purpose, but other polar liquids, such as acetone, methyl ethyl ketone and propylene carbonate, can also be used.

In order that the invention may be more fully understood, the following examples are given by way of illustration only. In these examples all parts are parts by weight per hundred parts by weight of polymer.

#### EXAMPLES 1-12

A series of low density polyethylene compositions (the polymer being that sold under the trade mark "Alkathene" XDG33) were prepared, the compositions containing various amounts of organophilic cation modified clays, and the dripping rate of the compositions and of the polymer without the additive, when heated to a temperature beyond the softening temperature, were determined.

The compositions were prepared as follows. The modified clay was added to toluene (in which the dispersant, where used, had previously been dispersed, if necessary with warming) and the mixture was stirred with a high speed stirrer for 5 minutes, methanol was then added and the mixture stirred for a further 5 minutes prior to colloid milling in a mill having a clearance of 0.002 inch. The resultant gel was stored in an oven at 90°C for 12 hours to remove the toluene and methanol.

The low density polyethylene was added to a mill and the previously prepared gel was added after the polymer had fluxed. The crepe was cross blended frequently and mixing was continued for 5 minutes. The crepe was cut off from the mill and pressed into sheets of  $\frac{1}{8}$  in. thickness. The mill temperature was 155°C and the pressing temperature was 145°C.

The dripping rate was determined on specimens having a length of  $4\frac{1}{2}$  in., a width of  $\frac{1}{2}$  in. and a thickness of  $\frac{1}{8}$  in. cut from the  $\frac{1}{8}$  in. thick sheets. Each specimen was marked by scribing three lines, respectively  $\frac{1}{4}$  in.,  $2\frac{1}{4}$  in. and  $4\frac{1}{4}$  in. from one end, thereon. One end of the specimen was clamped in a laboratory clamp positioned in a fume cupboard, with the longitudinal axis of the specimen horizontal and its transverse axis inclined at 45° to the horizontal. A pan of water was positioned below the specimen.

A standard  $\frac{3}{8}$  in. bunsen burner was ignited and adjusted with air ports open to produce a blue flame approximately 1 in. high. The free end of the specimen was ignited. When the flame reached the second mark,  $2\frac{1}{4}$  in. from the free end, the number of drips that fell in 15 seconds was counted and this was recorded as the dripping rate. (In Examples 9 to 12 inclusive, the specimens had a length of 6 in., a width of  $\frac{1}{2}$  in., and a thickness of 0.006 in., and each specimen was marked by scribing two lines, one at 1 in. and the other at 5 in. from one end of the specimen; the dripping rate determination was commenced 75 seconds after the flame had reached the

first mark and the number of drips that fell in 15 seconds was counted and recorded as the dripping rate).

Testing was discontinued after 3 specimens of the same composition had been tested and the dripping rate found to be within the following limits:—

0 — 5  $\pm$  1  
5 — 10  $\pm$  2  
10 — 20  $\pm$  3  
20 — 40  $\pm$  4

The average of the dripping rate for the 3 specimens is recorded in the following table.

The results obtained were as follows:—

Ex. No.	I Organophilic cation modified clay		II Dispersant		Ratio I : II	Dripping Rate
	Type	Parts	Type	Parts		
Blank 1	—	—	—	—	—	continuous
1	B.34	2	—	—	—	27
2	B.34	4	—	—	—	15
3	B.34	2	Paraffin wax	2	1:1	7
4	B.34	4	Paraffin wax	4	1:1	1—2
5	B.34	2	Polyethylene AC	2	1:1	12
6	B.34	4	Polyethylene AC	4	1:1	9
7	B.Sp	2	—	—	—	24
8	B.Sp	4	—	—	—	10
9	B.38	0.5	Paraffin wax	0.5	1:1	19
10	B.38	1	Paraffin wax	1	1:1	17
11	B.38	2.5	Paraffin wax	2.5	1:1	10
12	B.38	5	Paraffin wax	5	1:1	5

In this table: B.34 = dimethyldioctadecyl ammonium montmorillonite.

B.38 = dimethyldioctadecyl ammonium hectorite.

B.Sp = dimethyldioctadecyl ammonium sepiolite.

Polyethylene AC. = low molecular weight polyethylene.

In our Application No. 51680/64 (Serial No. 1,114,174) we have described and claimed polymer compositions comprising a polyamide, polystyrene or a polyolefin derived from a

straight chain olefin and, incorporated therein, one or more flame retardants and up to 10% based on the weight of the polymer, of an organophilic cation modified clay.

## WHAT WE CLAIM IS:—

1. A polymer composition which comprises, as major component, a synthetic thermoplastic polyolefin or polyamide and up to 10%, based on the weight of the polymer, of an organophilic cation modified clay. 20
2. A polymer composition according to claim 1, which comprises from 0.5, to 5%, based on the weight of the polymer, of organophilic cation modified clay. 25
3. A polymer composition according to claim 1 or 2, in which the organophilic cation modified clay is derived from a clay of medium or high exchange capacity, as hereinbefore defined. 30
4. A polymer composition according to any of claims 1 to 3, which additionally contains one or more anti-oxidants, stabilisers, anti-static agents, fillers and/or pigments.
5. A polymer composition according to any of claims 1 to 4, in which the organophilic cation modified clay is dimethyl dioctadecyl ammonium sepiolite, octadecyl ammonium montmorillonite, dimethyl dioctadecyl ammonium montmorillonite, or dimethyl dioctadecyl ammonium hectorite. 25
6. A polymer composition according to claim 1 substantially as herein described in any of the Examples.
7. Articles formed of a polymer composition according to any of claims 1 to 4 or 6. 30
8. Articles formed of a polymer composition according to claim 5.

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